

# Graphene oxide nano-domain formation via wet chemical oxidation of graphene



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## ABSTRACT

Chemical modification and functionalization of graphene is of great interest to alter its intrinsic properties. Among various methods, wet chemical oxidation is widely used for obtaining large quantities of graphene oxide or reduced graphene oxide. It is also often used as an intermediary step for further functionalization of the graphene. This work presents a microscopic study of the oxidation of single layer graphene on SiO<sub>2</sub>/Si substrate via wet chemistry. In addition to a uniform graphene oxide region growing at the edge, nano-sized graphene oxide domains within unoxidized graphene is observed. The graphene oxide nano-domain formation is attributed to the nonuniform impurity doping of the flakes which affect the local electrochemical reactivity of graphene. Graphene oxide nano-domain covered flakes which provide a long interface between the conducting graphene medium and the nano-domains, may be used as a template material for further functionalization to be used in novel electronic devices.

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## 1. Introduction

Graphene, the single layer honeycomb lattice of carbon atoms, has been the subject of intense attention over the last decade due to its unique electronic, mechanical and optical properties which pave the way for many potential applications including electronic devices, biosensors and composite materials [1–3]. Its superior electrical transport qualities [4] are, however, offset by the lack of an electronic band gap [5]. As a result, rather than working with pristine graphene, many researchers are concentrating their efforts on novel graphene derived materials which might allow for devices with tunable electronic properties. A few nanometer wide graphene ribbons, for example, have a bandgap opening that can be controlled by changing the width of the ribbon [6–8] whereas, hydrogenated graphene (that is graphane) [9,10], fluorinated graphene (fluorographene) [11,12] and graphene oxide (GO) [13,14] are insulators. Functionalization with diazonium salts is becoming popular as another route for controlling the electronic structure of graphene [15–19]. In addition to being a simple method for producing large amounts of graphene oxide, Hummers method [20] or

its modified versions [21,22] are also useful as an intermediary step for further functionalization of graphene [23]. GO is usually obtained by exfoliation of graphite oxide through sonication in a solvent [24]. There are, however, examples of direct oxidation of graphene, as well. For example, several groups used Atomic Force Microscope (AFM) lithography to induce local anodic oxidation on single and multi-layer graphene flakes [10,25–27]. More recently, Wang et al. showed that the single layer graphene (SLG) flakes on SiO<sub>2</sub>/Si substrates may be oxidized in a controlled fashion using wet chemistry [28]. Here, we microscopically investigate how the oxidation progresses on such flakes in detail during wet chemical oxidation. We show that the surface of the SLG does not get oxidized uniformly but start to oxidize first at the edges. Further, we observed formation of nano-sized graphene oxide domains near the oxide edges. It is demonstrated that in the case of few microns wide flakes preparation of graphene covered with GO nano-domains (GONDs) is possible. Such flakes may be used to study fundamental phenomena at the G/GO interface or as a template material for further functionalization to be used in novel electronic devices. The formation of the domains is attributed to the local increased reactivity within graphene due to nonuniform impurity doping from the substrate and adsorbates. Non-uniform reactivity might be at work in the reaction of SLG with other chemicals such as diazonium salts.

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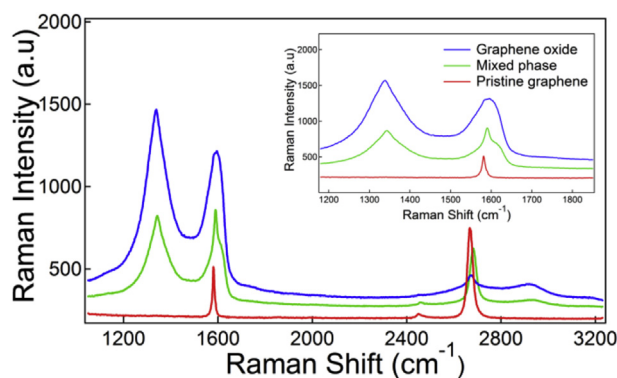
## 2. Experimental

Graphene samples were prepared by mechanical exfoliation method on SiO<sub>2</sub>/Si substrates using natural graphite flakes. Appropriate SLG are located under optical microscope and the number of layers is confirmed using a dispersive Raman microscope (Thermo Scientific, DXR Raman). Measurements were made using a 532 nm laser beam with a power ranging between 1 and 3 mW and 100× objective with estimated beam spot diameter of 0.6 μm. Despite having varying impurity doping levels, all samples used in this study had high crystalline quality with no D peak in the Raman spectra of the as prepared samples (see Fig. 1). The variations in the impurity doping levels within each sample were determined by recording Raman maps. In the Raman maps, image resolution was set either to 0.5 × 0.5 μm<sup>2</sup> or 1 × 1 μm<sup>2</sup>. During the mapping, Raman data is collected for 3s at each location on the sample. In the analysis of Raman spectra, graphene D, G and 2D peaks were fitted to Lorentzian peaks to identify parameters such as peak position, intensity and width before and after oxidation of the samples. Topographic and lateral force microscopy image of single layer graphene before and after chemical treatments were obtained by AFM (Park System, XE-series) in contact mode (AFM tip: APP Nano, SHOCONA-10). The AFM tip force was set to 4.9 nN. Conductive AFM (C-AFM) images are acquired using a Pt-Ir coated tip (Nanosensors, PPP-CONTSCPt) in contact mode with −50 meV tip bias relative to grounded sample.

For the oxidation of the samples we followed the recipe suggested by Wang et al. [28]. We prepared solutions of 0.015 M KMnO<sub>4</sub> in 50% H<sub>2</sub>SO<sub>4</sub> (1:1 vol ratio) and then the substrates containing graphene samples are immersed in these solutions for various durations. Immediately afterwards, substrates were rinsed with plenty of DI water. Often it is observed that the substrate surface is largely contaminated with chemical residues (presumably MnO<sub>2</sub> crystallites) after this procedure. These contaminants are effectively removed by immersing samples in 3% H<sub>2</sub>O<sub>2</sub> for 10 min. AFM images before and after H<sub>2</sub>O<sub>2</sub> treatment show no signs of structural changes to oxidized samples but the image quality improves upon the removal of the residues.

## 3. Results and discussion

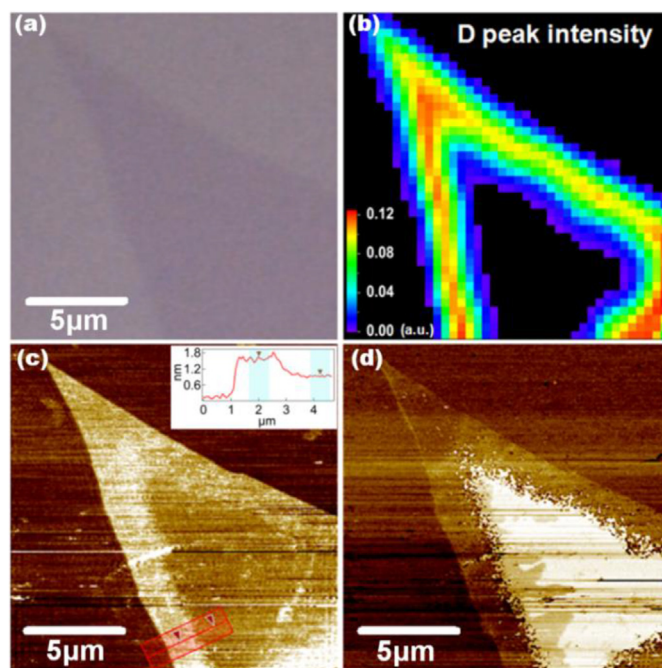
Raman spectroscopy is a versatile tool for investigation of graphene. It can be used to determine number of layers of few layer graphene [29–31], impurity doping level [32–34], edge type [35],



**Fig. 1.** Raman spectra of pristine graphene (red), partially oxidized graphene (green) and graphene oxide (blue). The presence of both a broad and a sharp peak at around 1580 cm<sup>-1</sup> in the partially oxidized graphene indicates the coexistence of both graphene and graphene oxide within the laser beam spot. (A colour version of this figure can be viewed online.)

strain [36], concentration of defects [37–39], and etc. In Fig. 1, we show three such Raman spectra obtained from a SLG, a completely oxidized graphene and a partially oxidized sample presenting peaks of both graphene and graphene oxide at the same time. On pristine graphene samples (red curve), the typical G band due to the first order scattering of the E<sub>2g</sub> mode and the 2D band due to the second order scattering of the A<sub>1g</sub> mode appear near 1580 cm<sup>-1</sup> and 2700 cm<sup>-1</sup>, respectively [40]. The 2D peak shape may be used as a fingerprint to identify the number of layers in graphene flakes [29–31]. The first order scattering of A<sub>1g</sub> (the D peak) is at around 1350 cm<sup>-1</sup> and is symmetry forbidden in ideal graphene. The absence of the D peak in pristine graphene is an indication of the high crystalline quality of the samples used in this study. Upon oxidation, some structural changes in the graphene lattice due to the formation of various oxygenated functional groups on the basal plane and at the edges are expected [22]. Formation of sp<sup>3</sup> hybridization by covalent chemistry and other structural defects result in the appearance of a strong D peak and a broader G peak [22] as seen in the Raman spectrum from the completely oxidized graphene (blue curve). The 2D peak in the same spectrum is much weaker and accompanied by other higher order peaks such as D + G. In some of our Raman spectra we came across a mixed phase, where sharp graphene and broad graphene oxide (GO) features are observed together in the same spectrum (green curve in Fig. 1). Similar features can also be seen in the work of Wang et al. but they do not discuss the reasons for such features [28]. We will explain the microscopic origin of such spectra further below.

Fig. 2 displays Raman D peak intensity map and contact mode topography and lateral force microscopy (LFM) images of a SLG flake oxidized via wet chemistry for 10 min as outlined in the experimental section along with its optical image prior to oxidation. The optical microscopy image (Fig. 2a) shows a typical contrast of graphene region relative to the substrate. Fig. 2b shows the D peak intensity as a function of position in the same region as the optical image (image resolution is 0.5 × 0.5 μm<sup>2</sup>) after the reaction.



**Fig. 2.** (a) Optical image of a pristine graphene prior to oxidation. (b) Raman map of D peak intensity, (c) AFM topography, and (d) LFM images after oxidation of the same sample for 10 min. via wet chemistry. Images indicate that the oxidation starts from the edges of the sample. (A colour version of this figure can be viewed online.)

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